
**OZONE TREATMENT
AND
TRACE ORGANIC CONTAMINANTS
IN DRINKING WATER**

FUTURE RESEARCH DIRECTIONS

Prepared for
Ontario Ministry of the Environment
Laboratory Services & Applied Research Branch
Environmental Technology Section

by

GORE & STORRIE LIMITED
CONSULTING ENGINEERS

JUNE 1984

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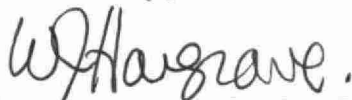
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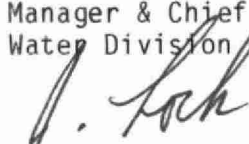
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We trust the information contained therein will be useful in assessing the present status of this topic and in establishing future research directions.

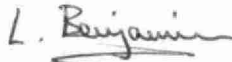
Yours truly,



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ABSTRACT

This report presents an in-depth literature review of the state of the art of ozone use in drinking water treatment. The report discusses the reactions and by-products resulting from the interaction of ozone with typical components of water, by-product removal and reduction, and presents a preliminary assessment of the health effects of by-products. Future research directions are identified.

ACKNOWLEDGEMENTS

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SUMMARY OF THE TECHNICAL DISCUSSION

The available literature has been reviewed and, from this, the following general observations are made:

1. The organic chemistry with ozone in aqueous systems is not well developed. Much of the work which has been done on "trace" organic compounds concerns their reaction kinetics and not the identification of by-products formed; consequently the conclusions here are directed toward a general interpretation and indications of the reaction directions.
 - Many of the studies done in organic solvent.
 - Many of the studies at "high" concentrations and a pH lower than that of raw water.
 - Hydroxy-hydroperoxides and peroxides, etc., have not been shown to be absent in water after ozonation; health effects need to be evaluated.
 - O_3 can react with olefins, acetylenes, aromatics, amines (e.g. ammonia, NH_3), sulfides, etc.
 - Direct ozonation (O_3) reactions with various organics span a rate range of 10^6 , with only two orders being fast enough to be applicable to conditions found in a water treatment plant.
 - OH (hydroxyl radical) reactions span a rate range of $\sim 10^3$.
 - O_3 can produce $HOBr$ from Br^- ; $HOBr$ can then form bromo-organics.
 - There is some preliminary evidence suggesting that chloride may be oxidized to hypochlorite in aqueous solutions. Whether or not this might lead to the formation of chloro-organics during ozonation of water has not been determined.
2. Ozonation reactors tend to be designed with an ozone transfer section and possibly a section for some additional retention time.

This type of design has a region with high ozone mass transfer which produces an ozone concentration in the water, which may be high or low, depending on the ozone reaction kinetics, and thereafter, a decrease in ozone concentration.

Most facilities control on the basis of some low ozone concentration in the effluent of the reactor. Indeed, there is usually no means of stripping ozone from the water; therefore, a low concentration must be maintained so as not to contaminate the plant working environment.

Indications from the chemistry are that sustained high aqueous phase ozone concentrations will be required to obtain significant reactions with many "trace" organics. This may be difficult and expensive in waters which have a high, relatively reactive ozone demand of background organic materials.

It is important to have an ozone reactor system which can provide and maintain high ozone concentrations.

Another indication from the reaction chemistry is that hydroxyl radical reactions are faster and less selective than ozone reactions; therefore, ozone reactor configurations with peroxide feed or UV irradiation, which increase hydroxyl radical production, will enhance "trace" organic removals.

Ozone reactors are very effective mass transfer units, and since many "trace" organic compounds are relatively volatile, concurrent air-stripping can occur with ozonization. Gas phase reactions of volatile organics and ozone are probable.

3. Ozone reaction by-product removal has not been extensively studied, but indications from the chemistry suggested that they should be more amenable to coagulation/flocculation and solids separation.

The by-products should be more biodegradable; therefore, GAC could become more effective due to bioregeneration of the active sites.

The by-products tend to be more water soluble, with lower molecular weights; therefore, physical separation processes, such as reverse osmosis, will be less effective.

4. The direct health implications of ozone by-products are largely unknown due to limited information on by-products and their concentrations. Indirect methods such as the Ames test, when applied to ozonated waters, have given variable results; that is, increases, decreases, or no changes in possible adverse effects in water quality have been reported.

SUMMARY OF FUTURE RESEARCH DIRECTIONS

The following have been identified as important areas for future research efforts in the application of ozonation to treatment of drinking water:

1. The nature and concentration of the by-products formed, with an emphasis on typical water treatment conditions. The reaction rate constants and by-products resulting from the reaction of ozone and hydroxyl free-radical with background organics, such as humic materials, is particularly important.
2. Conditions needed to minimize the formation of chloro-organics as a result of pre-ozonation and post-chlorination.
3. The potential, or lack of, for formation of chloro-organics during ozonation of chloride-containing waters.
4. Methods of ozone generation and mass transfer, such as electrolysis, which produce sustained, high ozone concentrations in water.
5. Methods of ozone generation and mass transfer which maximize the production of hydroxyl free-radical formation. Assessment of these methods in relation to "trace" organic removal and by-product formation is important.
6. The continued evaluation of the effectiveness of ozonation by-product removal by coagulation/sedimentation/filtration.
7. Continued development of procedures to assess the overall health quality of water, such as screening tests, are needed since the identification of all ozonation by-products and evaluation of their impact on health will not be possible.
8. The available screening test procedures typically involve examining the quality of water obtained by ozonating a much higher concentration of a

compound than normally found in raw waters or examining a concentrated extract. Further work should be undertaken to define the effect of concentration on the results.

9. The level of mutagenic activity of water appears to be a function of the extent of ozonation, i.e. ozonation results in an increase in mutagenicity to a peak value, followed by a decrease as the ozonation continues. This response should be investigated in detail.

INTRODUCTION

INTRODUCTION

The purpose of this report is to address gaps in the use of ozone technology for production of drinking water, which will then enable an effective assessment of future research directions.

The Terms of Reference for the work were provided in a Letter of Agreement with the Ontario Ministry of the Environment dated February 27, 1984. The Work Program from this Agreement is provided in Appendix B.

The subject was defined under four topic categories as follows:

- Typical reactions and resultant by-products due to interaction with diverse classes of "trace" organic compounds.
- Use of ozone in drinking water.
- Theoretical assessment of removal or reduction of reaction by-products.
- Preliminary assessment of health implications of the reaction by-products.

This task was primarily accomplished by a review and assessment of the current literature. The scope and degree of literature searched was somewhat constrained by the level of funding for the project.

It is important to note that this is not a report to outline appropriate design strategies but one to identify deficiencies in the available ozone technology. Having done this, it will provide direction for specific future research and will aid in policy decision making concerning the timing of this work.

It is a characteristic of all reviews that some interpretation of the available information be made, and this report is no exception. The predominant focus for this report was the application of ozone technology to existing conditions in Ontario water treatment plants. The reason for this was that Ontario has well-established waterworks facilities, and they represent an enormous capital

investment. Consequently, a goal of future research work would be to find ways of incorporating the findings into these existing water plants, therefore, a heavy weighting must be given to existing systems. Given this context, some of the available information is inappropriate here. For instance, many European ozone facilities utilize large raw or partially treated water empoundment areas. The ponds provide long retention times where biodegradation of ozonated organic compounds is possible. These reservoirs are a historical fact in Europe but not in Ontario; therefore, systems and associated information relating to this treatment step will have minimal importance for existing plants in Ontario so they are given little attention here.

This report is organized so that each of the previously mentioned topics is covered in a separate chapter. A complete understanding of the report results can only be obtained by reading all of the material, but a useful first reading is offered by the summary of findings in each chapter.

CHAPTER 1

OZONE REACTIONS AND BY-PRODUCT FORMATION

CHAPTER 1

OZONE REACTIONS AND BY-PRODUCT INFORMATION

1.1 Introduction

The objective of this chapter is to review the chemistry of ozone as it applies to drinking water treatment and to describe the by-products that result from the use of ozone.

1.2 Background Information on Ozone

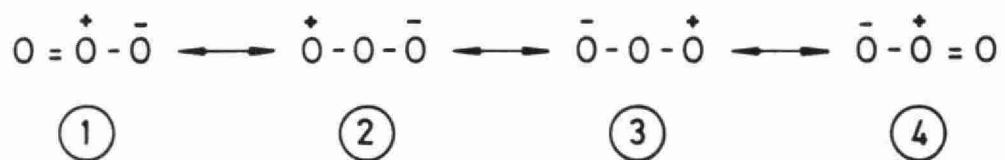
Ozone (O_3) is one of several possible forms (i.e. an allotropic form) of elemental oxygen. It is an extremely powerful oxidation agent, and its standard potential of 2.07 volts make it more powerful than chlorine (Cl_2 : 1.36 volts) and hypochlorous acid ($HOCl$: 1.47 volts). These standard potentials are for acidic solutions.

Ozone is considered to be an electrophilic reagent. An electrophile is a reagent which is electron-seeking. In contrast, a nucleophile is a reagent which is electron-donating. In the reaction of ozone with olefins, discussed below, the electrophile, ozone, attacks the electrons in the carbon-carbon double bond since these electrons are relatively accessible. The above definition of the term, nucleophile, means that, in this same reaction, the olefin is the nucleophile. As a result of ozone's electrophilicity, it tends to react with other electron-rich functional groups besides the carbon-carbon double bond, such as carbon-carbon triple bonds (acetylenes), the non-bonding pair of electrons on nitrogen and sulphur, and the bromide ion (Br^-). As will be discussed later, the latter reaction is responsible for the formation of brominated by-products during ozonation.

Ozone is represented by a hybrid of the "resonance" structures shown in Figure 1.1. The resonance structures are not real, but they serve to define the actual structure of the ozone molecule. The actual structure of the ozone molecule is a weighted average of the four structures shown. Even though structures 2 and

FIGURE 1.1

RESONANCE STRUCTURES FOR OZONE



3, also 1 and 4, are chemically the same, since it is not possible to distinguish between the two terminal oxygens, both are drawn because of the number of such equivalent resonance structures is used as one of the weighting factors to define the structure. The reactions of the ozone molecule can be rationalized as occurring via a 1,3-dipole (as in structure 2 or 3), or by an electrophilic reaction at the terminal electron-deficient oxygen (again, from 2 or 3).

1.3 Reaction of Ozone with Organics

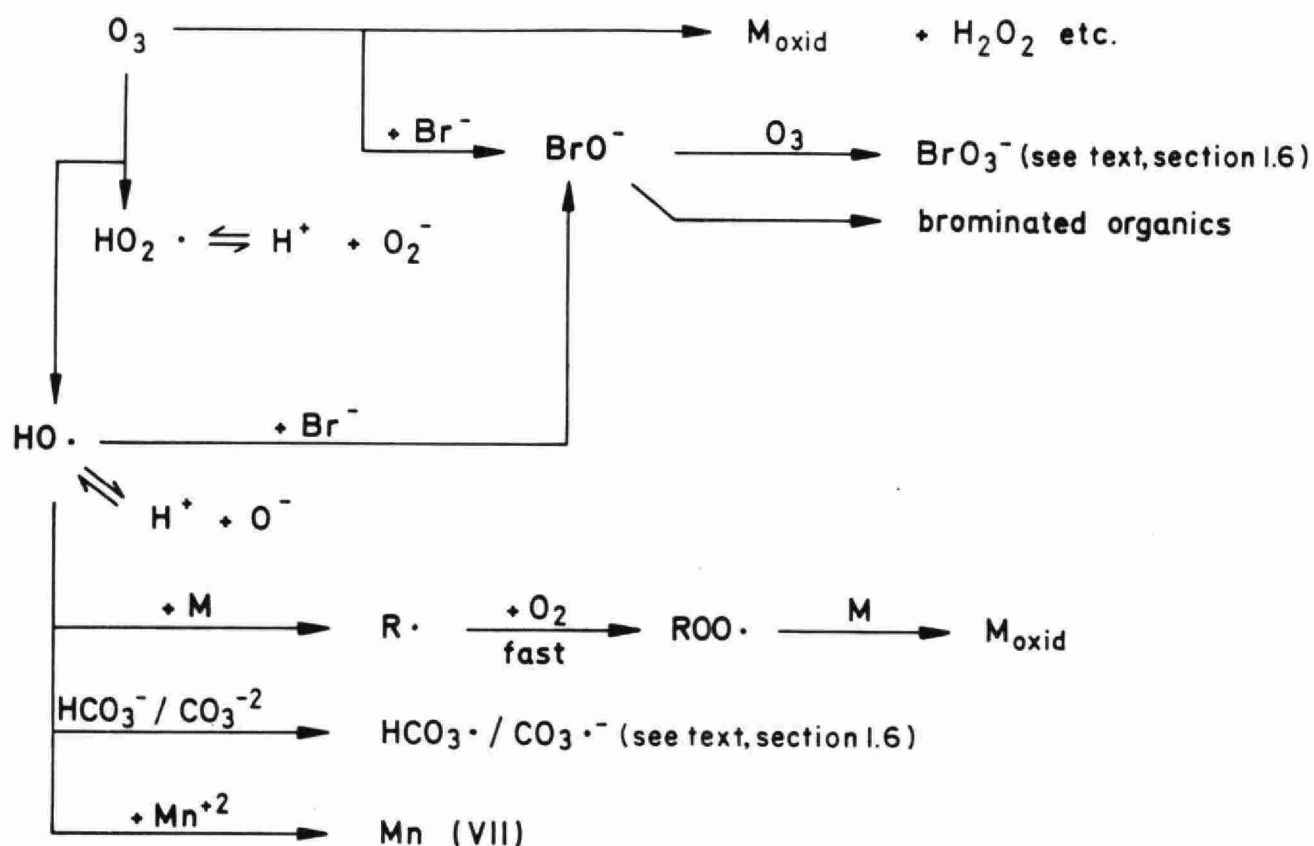
The reactions of ozone with organic materials in water have not been fully elucidated as yet, even though ozone has been used in water treatment for at least 80 years. The reaction of ozone with organic compounds in organic solvents has, however, been well studied. Generally, it is agreed that the knowledge of ozone chemistry developed from mechanistic and product studies in organic solvents is transferable to aqueous systems.

Reactions of the ozone molecule (O_3) with organics will be discussed in the following section of this chapter. These reactions will be classified as "direct" reactions since they involve the reaction of the reagent (ozone) with a substrate (e.g. phenol) before the reagent, ozone, is converted to a different species. Reactions of species which have been formed as a result of ozone reacting with other constituents of raw water, such as bromide ion (Br^-), or catalysts such as ultraviolet light (UV light), will be classified as indirect reactions. These will be discussed in another section of this chapter. Indirect reactions can make very important contributions to the overall chemistry which occurs during the application of ozone to a particular source of water.

Hoigné (1982) has summarized the secondary oxidants which can be formed during ozonation of raw water (see Figure 1.2). In this figure, M_{oxid} , M^1_{oxid} , etc., represent different oxidized products of the reaction of ozone (the reagent) with an organic compound (a substrate). In the following discussions, ozone will often be referred to as the "reagent", and the various compounds with which ozone reacts will be referred to as the "substrate".

FIGURE 1.2

SECONDARY OXIDANTS FORMED DURING OZONATION^a



M : represents an organic compound

M_{oxid} : represents an oxidized organic compound

a : adapted from Hoigne' (1982)

Before a more detailed discussion of the chemistry of ozonation of water is presented, it is appropriate to note that, in general:

- (a) The by-products of ozonation are less well defined than those of chlorination.
- (b) Many of the studies which report the nature of the by-products obtained as a result of ozonation were carried out in organic solvents and/or at substrate concentrations higher than those typically found in raw water.
- (c) The United States National Research Council (1980), (NRC), in "Drinking Water and Health, Vol. 2", states that it has "not been shown that many of the labile intermediates, such as hydroxy-hydroperoxides, peroxides, etc., are absent in ozonized organic solutions", and "these by-products may be of considerable significance to human health and need evaluating in this respect".

A listing of by-products that can be formed as a result of ozonating organics is given in Appendix A (Table A.1).

Due to the wide variety of organics that can be found in water, this list is not necessarily all-inclusive.

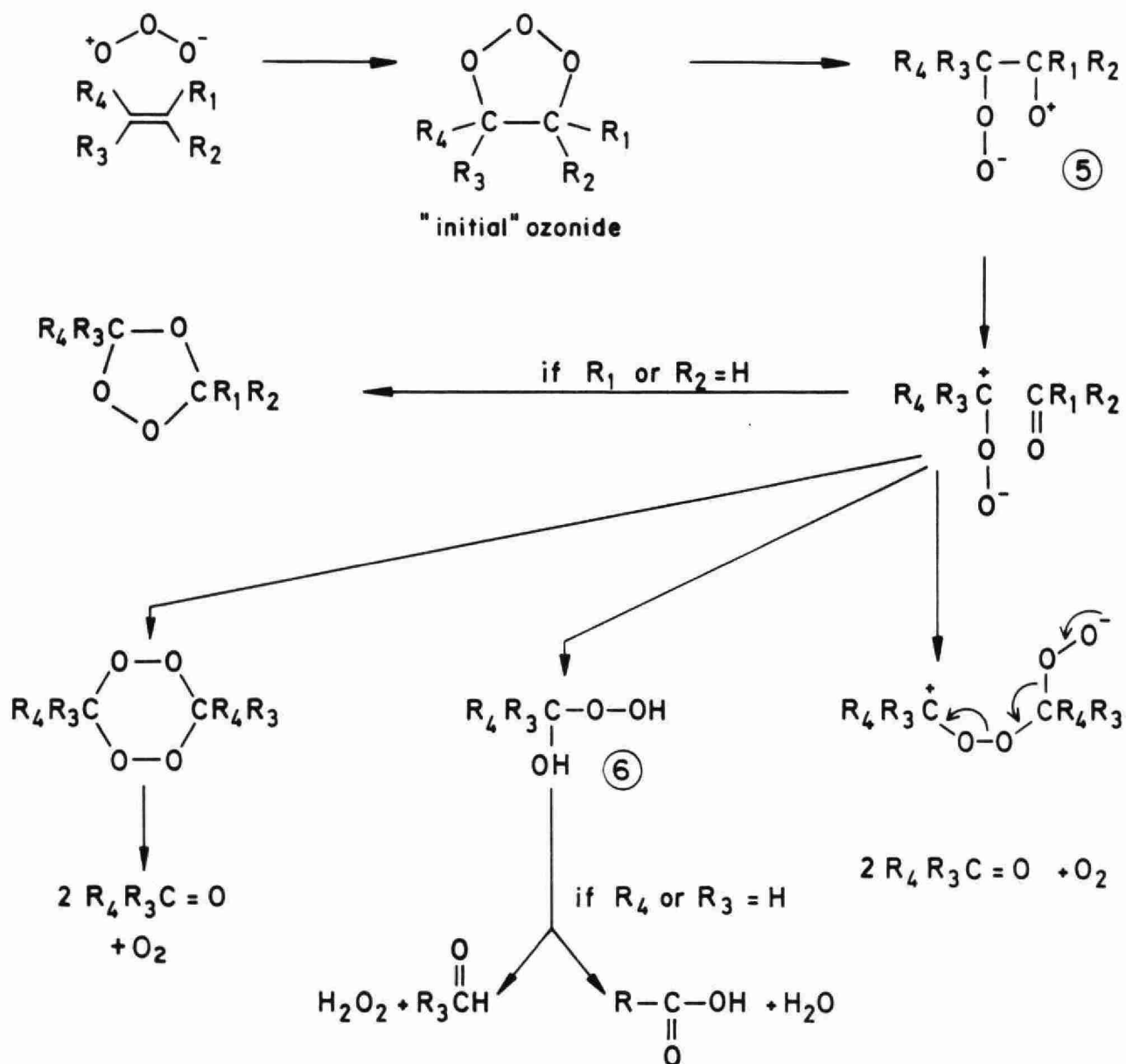
1.4 Direct Reactions

A large number of the direct reactions of ozone with organic pollutants in water occurs at the carbon-carbon double bonds of olefins and aromatics. The accepted mechanism of this reaction is based on the one proposed by Criegee, although some of the details of the stereochemistry of the conversion of the "initial" or "primary" ozonide (also called the "molozone") to the ozonide have not been elucidated (March, 1977). The basic mechanism is shown in Figure 1.3.

In aqueous media, the zwitterion (5) of Figure 1.2 mainly forms the hydroxy-hydroperoxide (6) (Oehlschlaeger, 1978). This species can either split

FIGURE 1.3

THE CRIEGEE MECHANISM FOR THE
DIRECT REACTION OF OZONE WITH OLEFINS^a



^a : adapted from March (1977) and Oehlschlager (1978)

out hydrogen peroxide (H_2O_2) to give an aldehyde or split out a molecule of water to give a carboxylic acid ($\text{M}(\text{C}=\text{O})\text{OH}$).

With certain hindered olefins, the reaction with ozone in organic solvents can lead to the formation of epoxides and epoxide derived by-products (see Figure 1.4). For example, the reaction of phenyl mesitylethylene (7) with ozone gives a 97% yield of the epoxide plus the aldehyde or vinyl alcohol, the latter two being in equilibrium with each other. (The aldehyde (8) will be the predominant form.) It has been shown (Bailey, 1972, and references cited) that the amount of epoxide formed increases with the bulk of the groups attached to the olefinic double bond. Bailey also reports that the epoxidation has not been studied in aqueous media but that the results would apply to aqueous ozonations.

In addition to the reaction with olefins, ozone is capable of reacting with acetylenes; carbon-nitrogen and similar unsaturated groups; nucleophiles such as amines, sulfides, sulfoxides, phosphines, etc.; and carbon-hydrogen bonds in alcohols, ethers, aldehydes, amines, hydrocarbons, etc. The reaction of these functional groups has been described by Bailey (1972), and a chart of the processes is presented in Figure 1.5. The reaction with carbon-carbon double bonds (olefins) is usually the most rapid of these functional groups, but nucleophiles such as amines and some carbon-nitrogen double bonds can approach or, in some cases, exceed the reactivity of a carbon-carbon double bond to ozone.

Hoigné (1982) has studied the rates of the direct reaction of ozone with organic compounds in water. The reaction rates are described by the following expression:

$$\frac{dN}{dt} = k [\text{O}_3] [\text{N}]$$

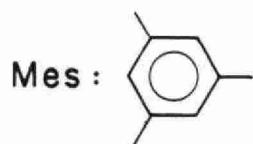
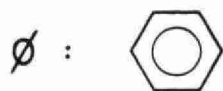
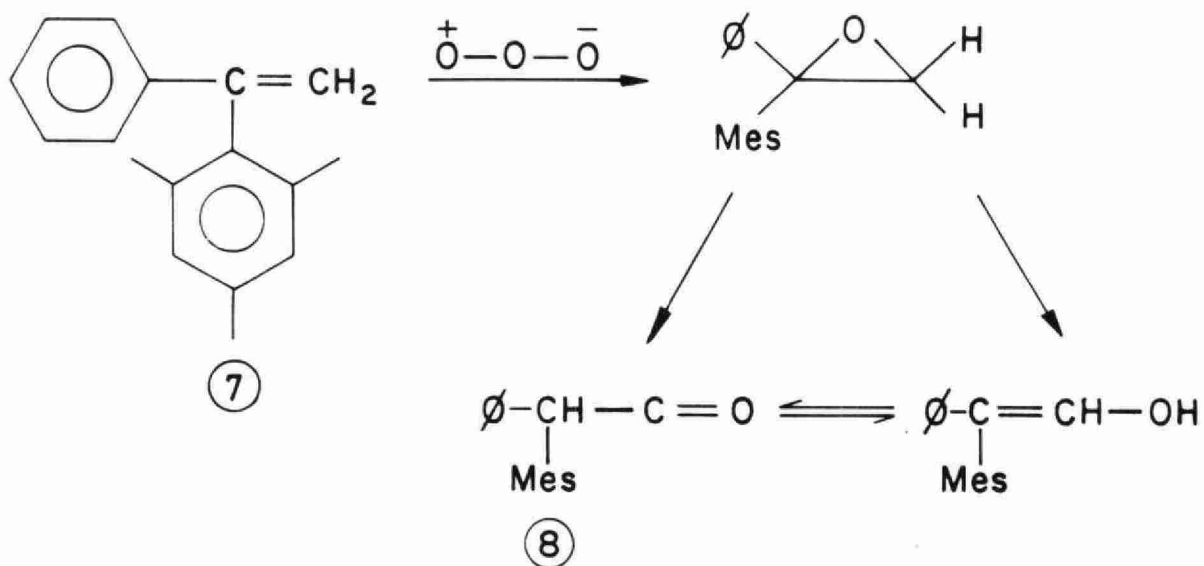
where

N = the organic compound of interest

Hoigné's rate data is presented in Table 1.1. As illustrated olefins are very reactive. Aromatics have lower reactivity. Benzene, for example, has a rate constant of about $5 \text{ M}^{-1}\text{s}^{-1}$. This results in a reaction time of 5,000 seconds

FIGURE 1.4

EPOXIDATION OF HINDERED OLEFINS BY OZONE^a



^a: from Bailey (1972)

FIGURE 1.5

Oxidation Products of Various Organic Functional Groups in Aqueous Medium(a)

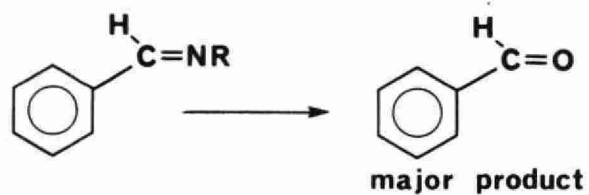
Acetylenes:



Aromatics:



Carbon-Nitrogen Double Bonds:



Amines:



Sulfides:



Sulfoxides:



Phosphines:



Phosphites:




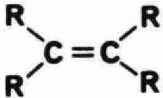
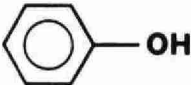
C-H Bonds:

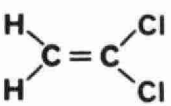
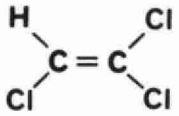
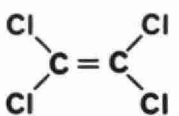
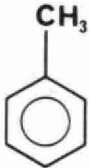
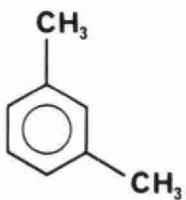


(a) : From Bailey (1972).

TABLE 1.1

Some Rates for Direct Reactions
Of Ozone with Organics(a)

COMPOUND	OZONE RATE CONSTANT(b) $M^{-1}s^{-1}$	TIME FOR 80% REDUCTION IN A COMPLETELY STIRRED REACTOR(b) (Minutes)
 (benzene)	5	83
 (olefins)	$\sim 2 \times 10^5$	<0.02
NH_3 (ammonia)	30	26
$R-\overset{\overset{O}{\parallel}}{C}-H$ (aldehydes)	13	17
$R^1R^2R^3C-OH$ (alcohols)	0.2	>1000
 (phenol)	$\sim 10^3$ for phenol(c) $\sim 1.4 \times 10^9$ for phenolate(c)	0.7 Practically instantaneous

 (1,1-dichloroethylene)	4000	<0.2
 (trichloroethylene)	17	40
 (tetrachloroethylene)	<0.1	>4000
 (toluene)	17	40
 (1,3-dimethylbenzene)	100	7

(a) : Adapted from Hoigné (1982); ozone concentration assumed to be 5 mg/L or 0.0001 M.

(b) : Values are approximate.

(c) : Rate constant for undissociated phenol is $10^3 \text{ M}^{-1}\text{s}^{-1}$; for the dissociated phenol (the phenolate), the rate constant was obtained by extrapolation (Hoigné, 1982). At pH 8, the combined rate constant would be about $2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$.

of 5,000 seconds (83 minutes) for an 80% reduction in concentration of a completely stirred reactor at the reaction conditions given in the table. For the same reduction in concentration, an olefin would require less than one second. The table also shows that compounds, such as ammonia (NH_3), organic aldehydes (R-CHO), and alcohols, would take from 400 to over 10,000 seconds (6.7 to 170 minutes) to be reduced in concentration by 80%.

Another trend in the data presented in Table 1.1 is the change in rates observed as various functional groups are attached to the olefinic or aromatic functional groups. For olefins, the rate of reaction decreases with increasing numbers of chlorine atoms. The double chlorine substituted olefin, dichloroethylene, is more than an order of magnitude slower than the non-chlorine substituted olefin. The tri- and tetrasubstituted ethylenes are four and five orders of magnitude slower to react than an olefin. For aromatic compounds, as exemplified by benzene and its derivatives, increased substitution by methyl groups (CH_3 groups) increases the rate of reaction. These trends are predictable on the basis of the mechanism of the reaction. Since the olefin and aromatic groups are being attacked by an electrophilic reagent, increasing substitution by electron-withdrawing groups (chlorine atoms) on the olefin will reduce the rate, while increasing substitution by electron-donating groups (methyl groups) causes an increase in rate. These types of trends can be used to estimate the reactivity of a compound if the reactivity of a related compound is known.

1.5 Indirect Reactions of Ozone in the Aqueous Phase

Raw water which is being used for the production of drinking water contains a variety of components which can react with ozone before the ozone can react with trace organic contaminants. Figure 1.2 shows some of the processes which convert ozone into other species which can react with the components present in water. These new species are thus responsible for the indirect utilization of ozone, and as a result of their reactions with the organic substrates present in the solution, increase the variety of by-products formed as a result of ozonation.

Of all the secondary oxidants found in water, the hydroxyl radical (HO^\bullet) seems to play a key role (Hoigné, 1982). Hydroxyl radicals are extremely reactive. Under alkaline (high pH) conditions, the hydroxyl radical has a standard potential of 1.4 volts compared to ozone, whose standard oxidation potential under alkaline conditions is 1.24 volts. As a result of the high reactivity, it shows very little selectivity. They are consumed in water within microseconds (Hoigné, 1982); however, their high reactivity may make them a significant pathway for the oxidation of organic compounds which are normally considered to be non-reactive towards ozone (as O_3).

Hoigné (1982) expresses the rate at which a solute M is oxidized by hydroxyl radicals, using the following equation to relate the disappearance of the solute to the amount of ozone decomposed (i.e. that portion of the total ozone that does not react as O_3 with substrates or is stripped off).

$$\frac{-dM}{dt} = \frac{-d(\text{O}_3)}{dt} \times \frac{[M]}{R}$$

where

O_3 = the amount of decomposed ozone

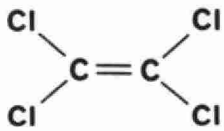
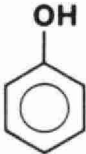
R = empirical constant for the solute M in a particular water. Functionally, R is the amount of decomposed ozone needed to reduce the concentration of R to 37% of the initial value in water. It does not depend on solute concentration under normal conditions. Hoigné reports that R is constant after the initial ozone demand of a water is met.

Table 1.2 displays some rate constants for the reaction of the hydroxyl radical with a number of organic substrates. The data given shows that there is only a ten-fold difference in reaction rate constant between tetrachloroethylene and phenol. For the direction reaction of ozone with these two substrates, there is a 10,000-fold difference in rate. This trend, that of a lessening of rate differences between organic substrates in the reactions with hydroxyl radical versus ozone, is a consequence of the high reactivity of the hydroxyl radical.

As mentioned previously, when a reactant such as hydroxyl radical has extremely high reactivity, the selectivity of the reactant is lessened. This means that

TABLE 1.2

Some Rates for Indirect Reactions
Of Ozone with Organics(a)

COMPOUND	HYDROXYL RADICAL RATE CONSTANT $M^{-1}S^{-1}$
 (tetrachloroethylene)	1.3×10^9
 (phenol)	1×10^{10}
$CH_3CH_2CH_2CHO$ (butyraldehyde)	2.5×10^9
$CH_3CH_2CH_2CH_2OH$ (butanol)	2×10^9
NH_3 (ammonia)	1×10^8

(a) : From Hoigné (1982).

the hydroxyl radical will react almost immediately after its formation with almost any species in its vicinity. Effectively, this results in its reaction with the first substrate it meets and makes the process of defining the full range of products much more difficult, if not impossible.

The hydroxyl radical (and the less reactive hydroperoxide, HOO^\bullet , which is also formed during the decomposition of ozone) will attack any carbon centre in an organic substrate having an active hydrogen or a double bond. The term "active hydrogen" basically refers to a hydrogen on a compound which is more reactive or labile. This is usually a result of a lower bond strength of that hydrogen to the carbon to which it is attached. Maggiolo (1978) provides an illustrative example of hydrogen abstraction, using benzene as the substrate (see Figure 1.6).

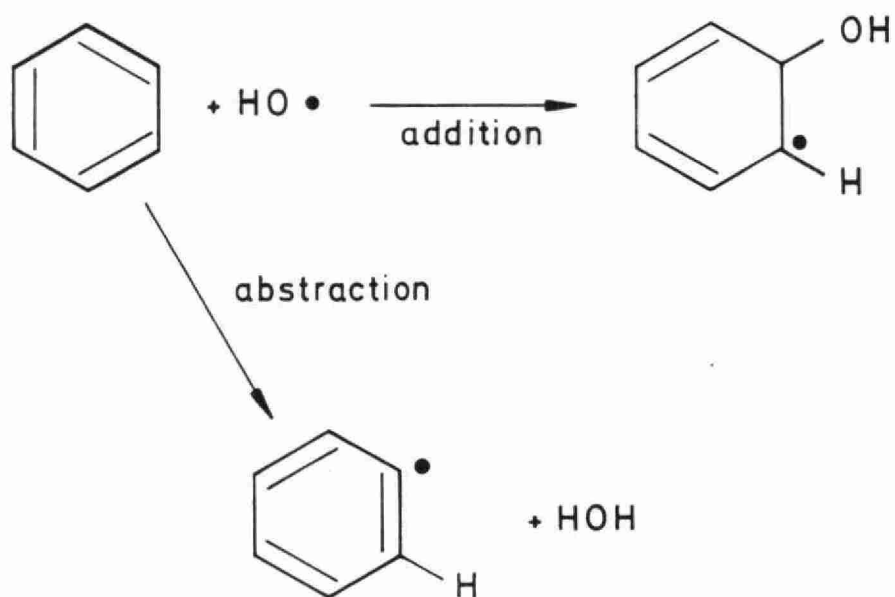
The radicals produced are able to react further to produce a variety of products. If the molecular structure bearing the hydrogen susceptible to abstraction is symbolized, R (R usually refers to an alkyl group, but the broader definition will be used here unless otherwise specified), the oxidation processes which can be initiated by the hydroxyl radical can be outlined using the following scheme shown in Figure 1.7 (Pryor, 1966).

The outline shown above is a generalized reaction scheme appropriate for summarizing the fate of the carbon-centred radical formed during autoxidation. Hoigné (1982) states that, while a new carbon-centred radical, $\text{R}^{1\bullet}$, could be formed and that chain reactions which lead to autoxidations may become operative, the usual situation in natural waters is that the reaction becomes quenched due to dissolved impurities.

Hoigné reports that, for most aqueous systems studied so far, only 0.4 to 0.5 organic molecules were oxidized per ozone molecule decomposed. The alkyl hydroperoxides (ROOH in the above scheme) formed during ozonation will break down to aldehydes, ketones, and alcohols (see Figure 1.8).

FIGURE 1.6

HYDROGEN ABSTRACTION BY HYDROXYL RADICAL^a



^a: from Maggiolo (1978)

FIGURE 1.7

OXIDATION PROCESSES THAT CAN BE
INITIATED BY THE HYDROXYL RADICAL^a

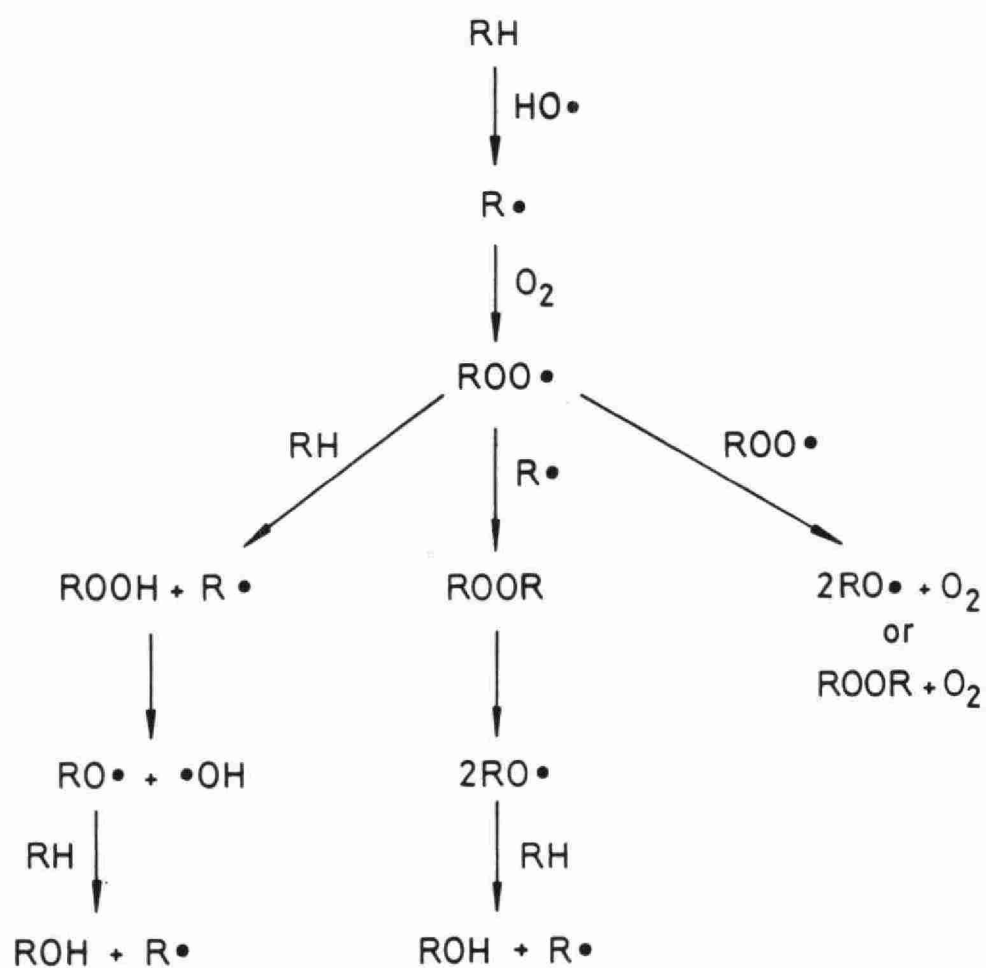
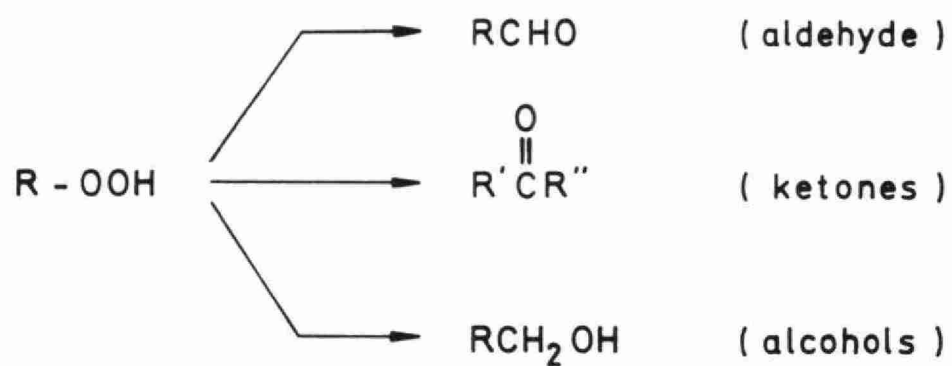


FIGURE 1.8

BREAKDOWN PRODUCTS OF ALKYL HYDROPEROXIDES



1.6 Oxidations of Other Species Present in Water

As mentioned previously, ozone is a very powerful oxidant. As a result, ozone can oxidize reduced forms of other oxidants in water. These, in turn, though not as powerful as ozone, can react with organic substrates to increase the variety of by-products formed as a result of ozonation. A good example is that of bromide.

Bromide (Br^-) is a reduced form of hypobromous acid, an oxidant. Haag and Hoigne (1983) have examined the kinetics of the oxidation of bromide under water treatment conditions. Their results are consistent with the scheme shown in Figure 1.9.

The first two steps result in a catalytic decomposition of ozone, and the third process results in the formation of bromate (see also Figure 1.2) from hypobromite. Bromates can produce methemoglobinemia. Masoud et al. (1973), as cited in NRC (1980), have estimated that the acute fatal dose of bromate is 57 mg/kg. Note that this results in the consumption of a further two moles of ozone.

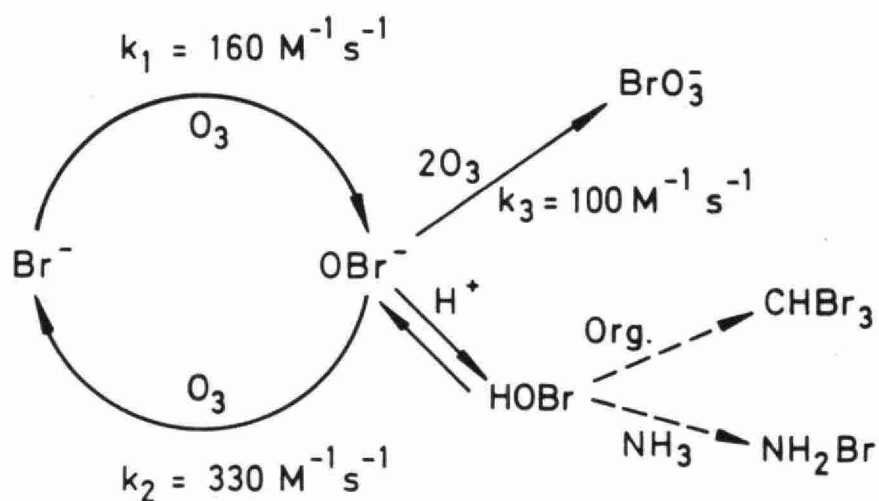
Of interest are the reports cited by Haag and Hoigne, stating that HOBr can produce potentially toxic brominated organics such as brominated phenols and bromoform. Note that the HOBr is formed from the base ^-OBr and that it is the HOBr which is the active brominating species. The base, ^-OBr , is a strong enough base to be at least 50% protonated at normal pH's of water (pK_a of HOBr = 8.7).

In a recent review, Cooper et al. (1984) report that bromide is oxidized by chlorine to hypobromous acid and hypobromite ion, while chlorine dioxide is not. These authors also report that monochloramine reacts with bromide to form bromochloramine (NHC1Br) but that no studies have been conducted to test whether NHC1Br produces THM's.

Since chloride (Cl^-) is in the same chemical family as bromide (both are halides) one must at least consider the possibility that chloride could be

FIGURE 1.9

REACTIONS OF OZONE WITH BROMIDE AND
HYPOBROMITE IN AQUEOUS MEDIA



a: from Haag and Hoigné (1983)

oxidized by ozone to hypochlorite (OCl^-). This would mean that chlorination reactions similar to those found during chlorination could occur. Williams et al. (1978) investigated the ozonation of chloride in seawater and in distilled water. In the ozonation of seawater, the oxidation of chloride to hypochlorite was not shown unequivocally to occur but was indicated by ultraviolet absorption at 293 nm, where hypochlorite is known to absorb ultraviolet light. In seawater, the absorption was transitory and unpredictable. In the ozonation of chloride in distilled water, the appearance of an absorption band at 293 nm was not found. Williams et al. report that the ozonation of hypochlorite is itself rapid and suggest that this might explain the transitory appearance of the hypochlorite absorption. The results obtained by Williams et al. do not prove that chloride is being oxidized to hypochlorite. They also do not answer the question of whether the hypochlorite, if found, is ozonated further before appreciable chlorination of organics can occur.

As illustrated in Figure 1.2, carbonate and bicarbonate radicals ($\text{CO}_3^{\cdot-}$ and $\text{HCO}_3^{\cdot-}$, respectively) can be formed during ozonation. Hoigné (1982) reports that, while these can be expected to behave as oxidants, their reactions are slow and their effects have not been observed in ozonated water.

1.7 Summary of Findings

- (a) The organic chemistry of ozone in aqueous systems is not well developed. Most of the work on trace organic compounds has involved reaction rates and not by-product formation and identification.
- (b) Most ozonation studies have been done at high concentrations for experimental convenience. Usually pH has not been controlled or even reported.
- (c) Most ozonation studies have been done in organic solvents. It is generally agreed that results obtained in organic solvents will be applicable to the direct reactions of ozone in water.

- (d) Hydroxy-hydroperoxides and peroxides, etc., have not been shown to be absent in water after ozonization; health effects need to be evaluated.
- (e) Ozone (O_3) can react with olefins, acetylenes, aromatics, amines, (e.g. ammonia, NH_3), sulfides, etc.
- (f) Direct ozonation (O_3) reactions with various organics span a rate range of 10^6 , with only two orders being fast enough to be applicable to conditions found in a water treatment plant.
- (g) Indirect ozonation (hydroxyl radical) reactions span a rate range of $\sim 10^3$.
- (h) Ozone can produce HOBr from Br^- ; HOBr can then form bromo-organics.
- (i) There is some preliminary evidence suggesting that chloride may be oxidized to hypochlorite in aqueous solutions. Whether or not this might lead to the formation of chloroorganics during the ozonation of water has not been determined.
- (j) Reactions of ozone (O_3) with competing substances, such as humics, ammonia, etc., that are present in raw water must be considered when using ozone for "trace" organics removal.

CHAPTER 2

OZONATION AS A UNIT OPERATION

CHAPTER 2

OZONATION AS A UNIT OPERATION

2.1 Introduction

Ozone is used in the treatment of drinking water to accomplish the following tasks:

- Disinfection - the inactivation of micro-organisms, including bacteria and viruses.
- Oxidation - the interaction of ozone with inorganic and organic materials to change their chemical state.

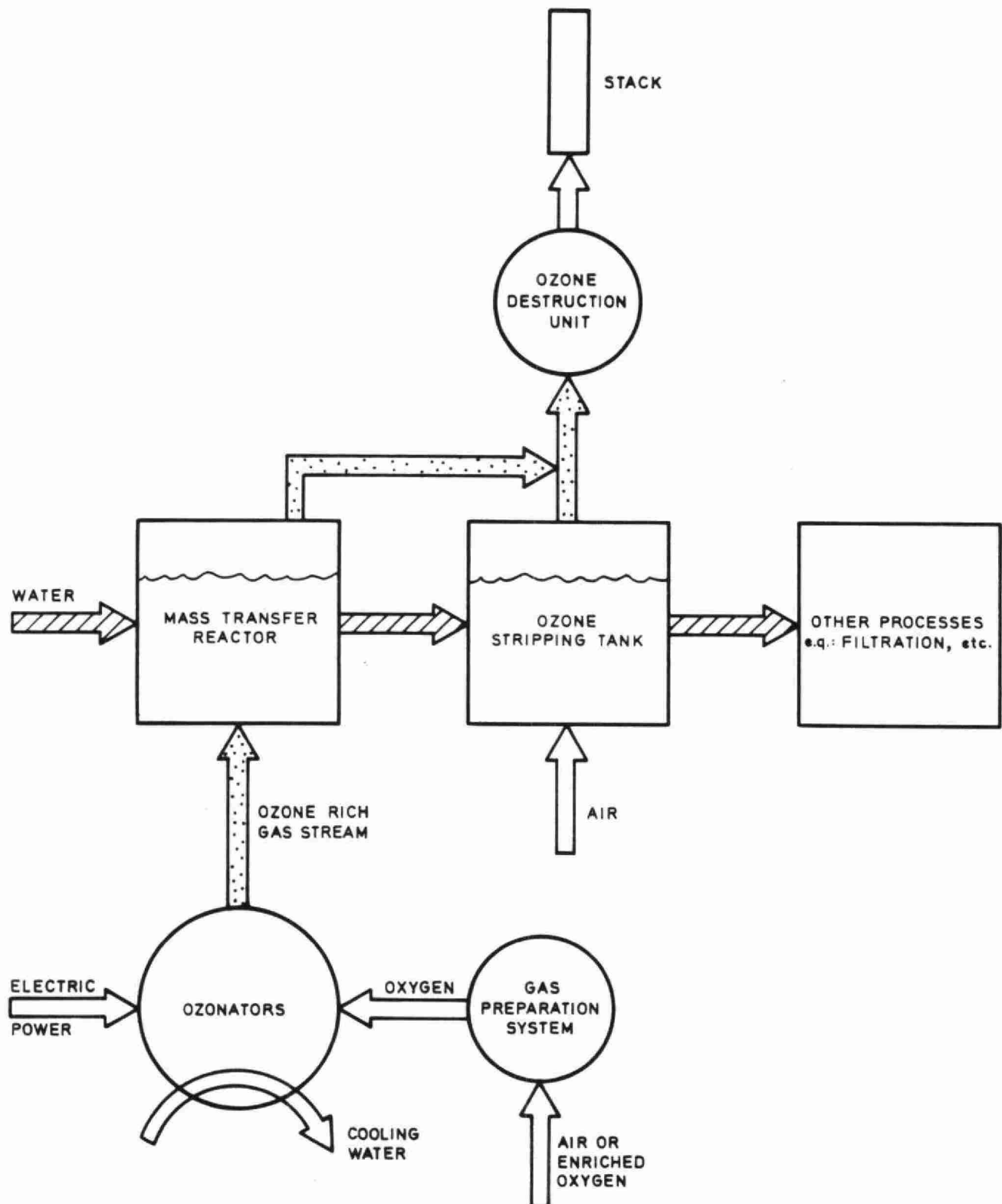
This facet of ozonation makes it useful for precipitation of some inorganic materials such as iron, the reduction of organic colour and odours, the oxygenation of organic compounds to increase their biodegradation, and in some cases, modifying organic compounds to provide organic precipitates.

In addition to the direct consequences of ozonation, some volatile organic materials can be removed during the transfer of ozone to and from the water.

The ozonation of water is accomplished by a system consisting of many parts. Figure 2.1 is a schematic representation of an ozonation system and illustrates the many components needed to produce the ozone, to transfer the ozone to the water, and to ensure the safe handling and disposal of excess ozone. As a means of organizing and elucidating information on the use of ozone, the major components of the system will be discussed separately.

The emphasis in this report is on the removal of "trace" organic materials. Consequently, much of the discussion will relate to optimizing ozonation systems toward removal of organic compounds at very low concentrations. One aspect of this concerns how ozone oxidation reaction rates can be increased 10- to 100-fold by combining ozonation and ultraviolet radiation procedures.

FIGURE 2.1
OZONATION SYSTEM SCHEMATIC



2.2 Ozone Generation

2.2.1 Ozonators - General

Ozone cannot be manufactured and stored because it is unstable; therefore, ozone must be generated on site as required. The following methods of ozone production have been used:

- Corona Discharge - consists of passing a dry oxygen-bearing gas, such as air, through a low-current electric arc (Chapsal et al., 1982).
- Ultraviolet Radiation - consists of passing a dry oxygen-bearing gas, such as air, through a beam of ultraviolet light (Masschelein, 1982).
- Electrolysis - consists of passing a low voltage current through an electrolyte from which ozone evolves and is collected in a passing gas stream (Masschelein, 1982 and Foller, 1982).
- Cheminuclear - consists of irradiating a high pressure, oxygen-rich gas stream with gamma radiation (Masschelein, 1982 and Steinberg et al., 1973).

Table 2.1 shows a comparison of these generation methods. The most widely used procedure is the corona discharge method because of the high relative energy efficiency. The electrolysis method, however, may represent a strong future contender because of the high ozone concentrations which enable improved mass transfer conditions (see Section 2.3, Reactors).

The ultraviolet method produces a low concentration ozone stream which has low mass transfer characteristics; consequently, the UV method has limited application for large systems unless the synergism between ozone and UV in the aqueous phase, and the ozone generation in the gas phase, can be integrated (see Section 2.3, Reactors).

The cheminuclear generation method will only be applicable to very large facilities, and then, not in the foreseeable future.

TABLE 2.1

Comparison of Ozone Generation Methods

GENERATION METHOD	PRODUCTION ENERGY REQUIREMENTS (g O ₃ /kWh)	TYPICAL OZONE CONCENTRATION (%O ₃ by wt. in gas)	COMMENTS
Corona Discharge	60 to 100	1 to 2 (possibly 4% with oxygen)	Most prevalent
Ultraviolet	0.3 to 1.8	0.02 to 0.97	Possible synergism between ozone and UV in water
Electrolysis	30 to 80	10+	Experimental, but with future possibilities
Cheminuclear	high	high	Experimental, probably very large systems with oxygen fed

Theoretical thermodynamic energy required to produce ozone from oxygen is: 1030 g O₃/kWh.

Sources: Masschelein (1982), Chapsal et al. (1982), Steinberg et al. (1973), Foller (1982).

2.2.2 Corona Discharge Ozone Generators

Some of the factors controlling the production of ozone from a corona are given by the following relationships (Evans, 1972; see also Fisher et al., 1984).

$$M \propto F \cdot E \cdot V^2/D \quad (2.1)$$

where

- M = yield of ozone/unit area of electrode
- F = frequency of applied voltage
- E = dielectric constant of layer
- V = peak discharge voltage across the gap
- D = thickness of the dielectric layer

and

$$V \propto P \cdot G \quad (2.2)$$

where

- P = gas pressure in the gap
- G = gap width

Other factors which control the production of ozone are temperature, flow rate, oxygen content, and moisture content of the gas feed. With optimum operating conditions, typically, 1% and 2% ozone (by weight) can be produced in air and pure oxygen feed streams, respectively (Chapsal et al., 1982). Ozone concentrations of 4% to 6%, however, are possible in some systems with air and oxygen, respectively (Fisher et al., 1984).

It is essential that the gas feed and the conducting electrodes be maintained at a controlled and uniform temperature, otherwise the ozone yield can be markedly reduced.

The corona discharge ozone generation method can produce ozone in either air (20% oxygen) or enriched oxygen streams (greater than 20% oxygen). In either case, the gas stream entering the ozonator must contain very little water vapour, otherwise the ozonator efficiency is greatly reduced. The moisture content must be maintained at a dew point of about -60°C , which represents about 0.01 gm water per cubic metre of air.

Ozonator manufacturers attempt to optimize the many factors above to satisfy the following criteria:

- Lowest capital cost
- Lowest operating cost
 - Power consumption
 - Maintenance
- Long life expectancy for the equipment

As will be discussed later, two additional criteria, gas pressure and ozone concentration, are very important to the transfer of ozone from the gas stream to the water. Since many of the controlling factors and desired criteria are contradictory, each ozonation system must be designed with a specific blend of these conditions. It is only through a detailed assessment that the proper emphasis of these many conditions can be found for a particular application.

2.3 Reactors

Under this heading, the following items will be discussed:

- Mass transfer of ozone to and from the gas phase and the water phase, including the effects of ozone demand
- Reactor configurations
 - Effect on the stripping of volatile organic materials from the water during the ozone transfer operation
 - Effect of synergism between ozone, hydrogen peroxide, or ultraviolet irradiation

Figure 2.1 shows two reactor components: the ozone mass transfer tank and the ozone stripping tank. The mass transfer reactor is where the ozone is introduced into the water from the ozone-rich gas coming from the generator. The ozone stripping tank is where the excess ozone is removed from the water to prevent ozone contamination of the plant. The off-gases from each tank will contain ozone which, in some cases, can be re-introduced into the water, but ultimately, an ozone-rich gas stream must be discharged. The discharged gas

must be treated to ensure that ozone levels are sufficiently low to meet air quality guidelines.

2.3.1 Equilibrium Ozone Concentration

For water in direct contact and at equilibrium with a gas phase containing ozone, the concentration of ozone in the water can be expressed by the following relationship:

$$C_w = P \cdot C_g / H \quad (2.3)$$

where C_w = equilibrium concentration of ozone in water (kg/m^3)
 P = gas pressure (atmospheres)
 C_g = equilibrium concentration of ozone in gas (kg/m^3)
 H = Henry's Law constant (atmospheres)

Table 2.2 shows the Henry's Law constant and the equilibrium ozone concentration data for pure water as a function of temperature.

It is important to note the low values of the aqueous phase ozone concentrations. Also, it is important to understand that the aqueous phase ozone concentrations can only be maintained if the water is in contact with a gas containing ozone at the respective concentration.

In all practical applications, the instant the water is removed from contact with the ozone-bearing gas, the ozone concentration in the water will start to decrease. The decrease will occur by exchange of ozone to the atmosphere, spontaneous decomposition of the ozone, and/or reaction of ozone with materials contained in the water.

2.3.2 Mass Transfer of Ozone into Pure Water

The exchange of ozone from the gas leaving the ozone generator into the water to be treated is an essential and major function in ozonation. The mass transfer of ozone into pure water can be described by the following equation:

TABLE 2.2
Equilibrium Ozone Concentration Data
For Pure Water

WATER TEMPERATURE (°C)	HENRY'S LAW CONSTANT		EQUILIBRIUM OZONE CONCENTRATION IN WATER (mg/L) AT ATMOSPHERIC PRESSURE	
	(2) (mg O ₃ /L gas) (mg O ₃ /L water)	(1,3) (atm)	(4) 1% O ₃ in Gas	(4) 2% O ₃ in Gas
0	1.60	1940	7.9	15.9
5	1.81	2180	7.1	14.0
10	2.04	2480	6.2	12.5
15	2.35	2880	5.4	10.8
20	3.08	3760	4.1	8.2
25	3.54	4570	3.6	7.2
30	4.44	5980	2.9	5.7

NOTES:

1. From the International Critical Tables (Perry, 1963).
2. Calculated from (1) using multiplier = $18 \times \text{density air} \div 28 \times \text{density water}$.
3. Roth and Sullivan (1981) provide a correlation which indicates pH dependency:

$$H = 3.84 \times 10^7 [\text{OH}^-]^{0.035} \exp [-2.428 \times 10^3/T]$$

where H = Henry's Law constant (atm)
 $[\text{OH}^-]$ = hydroxide molar concentration
T = temperature in °K = (°C + 273.15)

At a pH of 7.0, this correlation provides Henry's Law constants which are 25% to 50% higher than the values shown in the table above.

4. Ozone concentration in the gas by weight at a standard temperature and pressure of one atmosphere and 20°C, respectively.

$$N = k_L \cdot a (P \cdot C_g/H - C) \quad (2.4)$$

where

- C_g = ozone concentration in carrier gas (kg/m^3)
- N = rate of ozone transfer (kg/s)
- C = ozone concentration in bulk water (kg/m^3)
- k_L = mass transfer coefficient (m/s)
- a = gas/water interfacial area (m^2)
- P = pressure of ozone carrier gas (atm)
- C_g = ozone concentration in carrier gas (kg/m^3)
- H = Henry's constant (atm)

This equation represents the two film theory with Henry's Law and recognizes that the liquid film controls. This means that an assumption is made that the layer of water next to the water/gas interface is always saturated with ozone (Rice and Netzer, 1982; Roustan and Mallevialle, 1982; and Treybal, 1968). The utility of equation 2.4 is quite limited because generally it does not account for decomposition and reaction of the ozone in the water phase.

2.3.3 Mass Transfer of Ozone with Chemical Reactions

Equations have been developed to consider simultaneous mass transfer and chemical reactions (Rice and Netzer, 1982 and Roustan and Mallevialle, 1982). Usually the spontaneous decomposition of ozone and the reaction of ozone with a constituent in the water are considered to be a pseudo first-order reaction with respect to ozone. The effects of chemical reactions are often correlated by the acceleration or enhancement factor, E ; which is the ratio of mass transfer coefficients, k_L , with and without the chemical reaction. Thus, E has values which range upward from 1.0. $E = 1.0$ represents a condition without chemical reaction. $E = (D \cdot K/k_L^2)^{1/2}$ represents an upper bound when the reaction rate is much faster than the liquid film diffusion; where D is the diffusivity of ozone in water ($0.2 \text{ m}^2/\text{s}$ at 20°C [Lyman et al., 1982]), k is the first-order reaction rate constant (s^{-1}), and k_L is the liquid film mass transfer coefficient (m/s).

A very important aspect of mass transfer conditions with chemical reactions is that the ozone concentration in the water may be low or zero. This results when the ozone is consumed at a rate which approaches the rate at which the mass transfer system can supply ozone. Clearly, the limit of this occurs when the sum of the chemical reaction rates is faster than the rate of ozone diffusion across the gaseous/liquid film. Under these circumstances, the ozone concentration in the water will remain at zero until the reacting species in the water are consumed. The reaction of interest, for instance the reaction of a toxic trace organic with ozone, may represent a very small fraction of the total chemical reactions at any time. Consequently, the rate of the reaction of interest may be very low due to low ozone concentrations that result from competitive reactions with relatively fast reacting high concentration background materials in the water.

As already discussed in Section 1, the removal of trace organic compounds may be quite slow due to low reaction rate coefficients and low substrate concentrations. Thus, in addition, the low ozone concentrations due to competitive reactions will undoubtedly reduce the rate of trace organic removals. Clearly, therefore, it is as important to understand the competitive reaction rates as the reaction of interest so as to understand how to design a system to ensure suitable retention times and ozone concentration in the water phase.

2.3.4 Ozone Stripping

Figure 2.1 illustrates an ozone stripping tank following the ozone mass transfer unit. The purpose of the stripping tank is to remove residual ozone from the water so it will not contaminate the remaining working environment of the plant. If the ozone concentration leaving the mass transfer reactor is zero at all times, then this unit process is not needed; however, when the design goal is to maintain high ozone concentrations throughout the entire reaction period, such as with trace organic removal, this process step becomes increasingly important.

2.3.5 Volatile Organic Stripping

As discussed above, Figure 2.1 shows two gas/liquid phase mass transfer reactors. The first is to impart ozone to the water and the second is to remove the residual ozone. Each of these unit processes have the potential to remove volatile organics from the water phase. The factors discussed in Section 2.3.1 for ozone equally apply to any volatile component; therefore, the steps taken to ensure good ozone transfer could also ensure good transfer of volatile organics from the water to the gaseous streams.

Depending upon the nature of the organic constituents in the water, it may be worthwhile to consider the stripping operation as an integral part of optimizing a system design. The aspect of organics removal from the gaseous stream should be considered including the reactions with gaseous ozone.

2.3.6 Combined Reactors

As noted in Chapter 1, many chemical reactions benefit from synergisms between ozone and hydrogen peroxide or UV radiation. The results are reduced specificity of reaction and increased reaction rates.

Some work has been done to evaluate the combining of ozone and UV reactors (e.g. Prengle, 1983). Given the potential benefits from this type of work, much more should be done.

2.4 Treatment of Ozone-Rich Off Gases

As mentioned above, the off-gases from the ozone mass transfer reactor and the ozone stripping tank will contain ozone. The ozone in these gas streams must be reduced to levels which meet air quality guidelines (e.g. 0.1 ppm).

Ozone destruction in air is usually accomplished by high temperatures or a combination of a catalyst and elevated temperature (Treybal, 1968).

Table 2.3 shows the rate of thermal destruction of ozone versus various temperatures. Most systems operate in the 250°C to 300°C range. These systems are operating cost intensive due to the heating of the gas stream.

The catalysts for ozone destruction are often based on palladium and the optimum operating temperatures seem to be about 30°C to 40°C. This system tends to be capital cost intensive.

2.5 System Cost Estimates

Figure 2.2 shows the capital and annual costs for a range of daily ozone productions.

These cost curves are provided so a comparison can be made between ozonation and other methods of treatment; however, these data must be used judiciously because the costs of the ozonation systems are very dependent on the objective of the design. For instance, disinfection systems with relatively low ozone dosage and low contact time will have lower costs than a system designed to maintain near-saturation ozone dosages for a very long time.

2.6 Summary of Findings

- (a) Many ozone systems have proven to be surprisingly undependable and difficult to maintain. The reliability of present ozonation systems is very dependent on the adequate design of the entire system, particularly the gas feed preparation system and the ozonators.
- (b) The effectiveness of trace organic removal will be largely controlled by the gas to liquid transfer of ozone and the resultant ozone concentration in the water.
- (c) The theoretical limit for ozone concentration in water is dependent on the ozone concentration in the gas.

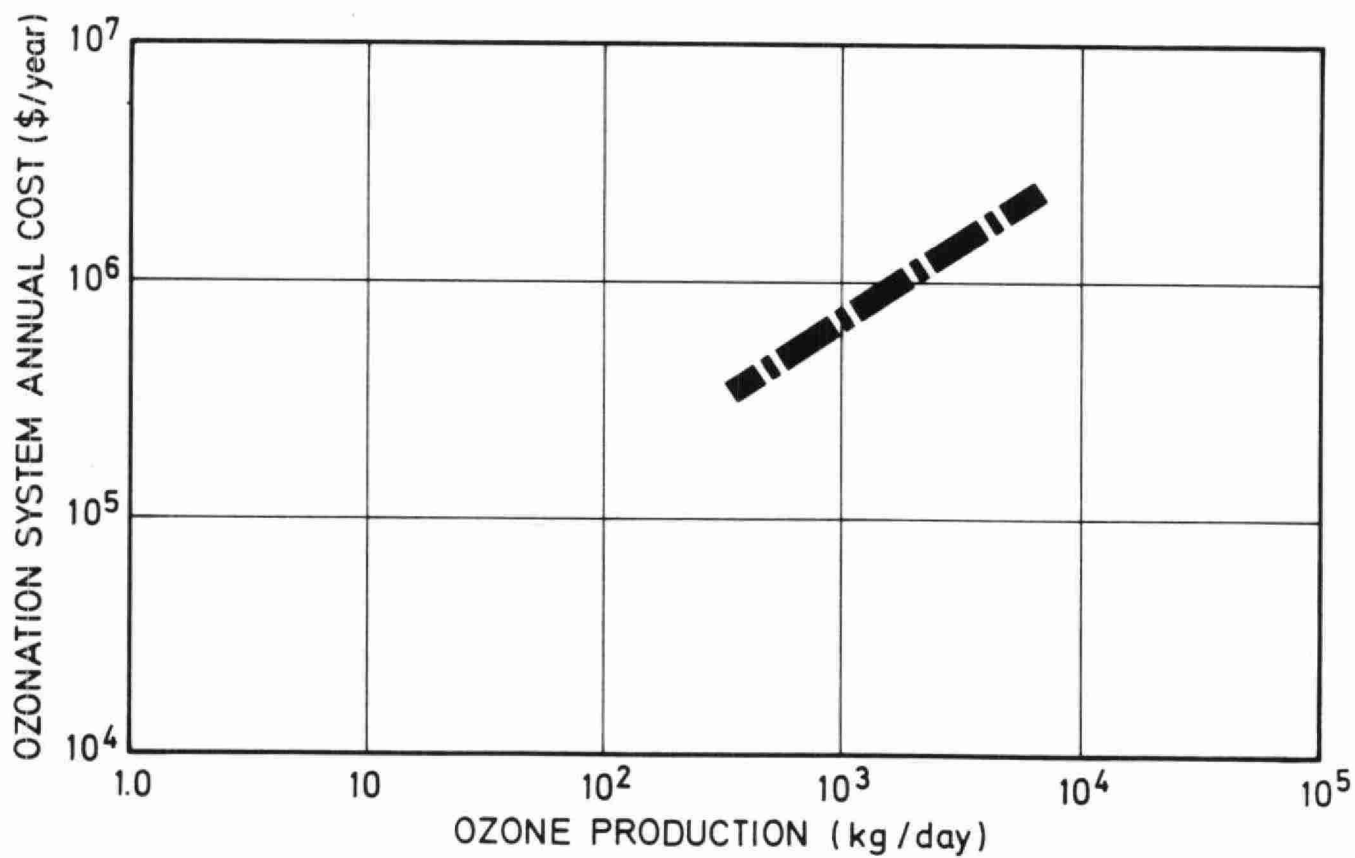
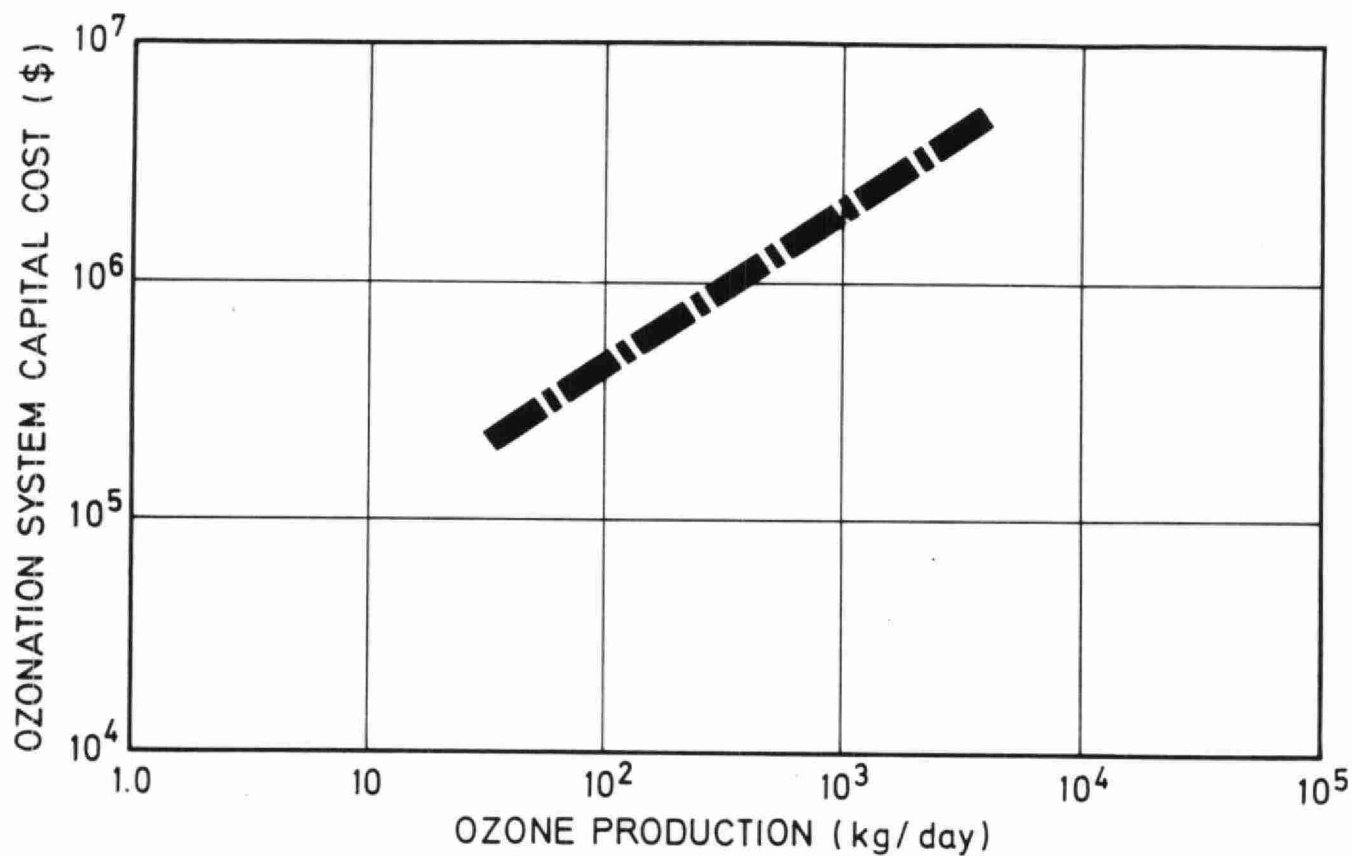
TABLE 2.3
Thermal Decomposition of Ozone

TEMPERATURE (°C)	EFFECTS
30	Thermal decomposition starts
40	Significant disposition
200	70% reduction in 1 minute
230	95% reduction in 1 minute
300	100% reduction in 2 seconds

Source: Prengle et al., 1977

FIGURE 2.2

ANNUAL AND CAPITAL COSTS
FOR OZONATION SYSTEMS



Corona discharge-type ozonators presently used set the limits of ozone in the gas phase at 1% to 2%, but concentrations as high as 4% to 6% may be economically feasible under certain circumstances. However, electrolysis production methods may be commercially available soon, which could increase the gas phase concentration.

- (d) The theoretical limit of ozone concentration in water can be significantly reduced by chemical reaction with other constituents in the water and the spontaneous decomposition of the ozone. Thus, from the standpoint of "trace" organic removal, the sum of all other competitive reactions consuming ozone becomes important because the ozone concentration may remain low.
- (e) Removal of "trace" organics will require high ozone concentrations in the water, and this will result in by-product gas streams with high ozone concentrations; thus, the gas streams will require very effective treatment to continuously meet air quality guidelines.
- (f) Ozone transfer units will effectively strip many volatile "trace" organic compounds. Gas phase organic control may be necessary to meet air quality guidelines.

CHAPTER 3

BY-PRODUCT REMOVAL AND/OR REDUCTION

CHAPTER 3

BY-PRODUCT REMOVAL AND/OR REDUCTION

3.1 Introduction

The objective of this chapter is to review current knowledge about organic by-product removal and to suggest areas where more research should be directed.

As previously discussed, the ozonation of natural water produces a variety of by-products. While most of these appear to be innocuous, in some cases, new substances which may be of concern from a public health viewpoint are produced or freed from complexation by ozonation.

Because it is not known what the public health effects of the ozonated by-products would be, and because tests to determine these effects would be expensive and take a long time, it is assumed that ozonated organics should be removed to below detectable limits, or as much as possible with available technology.

From a review of the literature, it is evident that work done on ozonated organics so far has concentrated on identifying the compounds formed. To date, research has focused on removal or reduction of chlorinated organics; little work has been done on removal or reduction of ozonated organics. As a result, much of this chapter relies on the foundation of work done on removal or reduction of chlorinated organics.

3.2 Chemistry

The detailed chemistry of ozone by-product formation was discussed in Chapter 1. Briefly, however, when ozone is added to water containing organic chemicals, the following reactions take place:

Step 1 - Organics + O₃ → By-products (INITIALLY)

Step 2 - By-products + O₃ → CO₂ + H₂O + Cl⁻, etc. (ULTIMATELY)

Kinman et al (1978) noted that Water Treatment Step 2 may not take place to any great extent. This is because of:

- Insufficient time
- Difficulty in obtaining a high ozone concentration
- pH and other factors may not be optimum

Other methods, therefore, must be considered for by-product removal or reduction. The two basic methods are: (1) prevention of formation, i.e. removal of organics before they can react with ozone, and (2) removal of by-products once formed by existing or new unit process. Whichever method is chosen, the problem still boils down to one of organic removal/reduction, either as raw water water organics or by-products.

A first step in studying organic by-product removal is to examine the effectiveness of existing unit process used in water treatment. Subsequent steps could include investigations of unit processes not currently used in water treatment and optimization of each process for organic by-product removal.

The unit processes presently employed in water treatment include the following groups:

1. Coagulation/flocculation
Sedimentation
Filtration
2. Solid-phase adsorption with: powdered activated carbon (PAC)
granular activated carbon (GAC)
resins
3. Gas phase or air stripping
4. Reverse osmosis

Figure 3.1 relates compound characteristics to general trends for removal by these processes for both ozonated and non-ozonated materials.

FIGURE 3.1

General Trends for Organics Removal of Ozonated
and Non Ozonated Organics

	NON-OZONATED ORGANICS	OZONE (O ₃) →	OZONATED ORGANICS
Relative Organic Compound Characteristics	Non-polar Non-oxygenated High molecular weight		Polar Oxygenated Low molecular weight
Effect of Organic Compound Characteristics on Potential Treatment Processes	Lower biodegradation Higher absorption Better air stripping Poorer coagulation		Improved biodegradation Less absorption Poorer air stripping Better coagulation

The unit processes in Group 1 are common to most water treatment plants in Ontario. In contrast, the unit processes in Groups 2, 3, and 4 are not frequently seen. The discussion below will review the potential of the unit processes listed above for reduction or removal of organic by-products.

3.3 Coagulation/Sedimentation/Filtration

Along with disinfection, these are the most commonly used unit processes in water treatment. According to Rice (1980), organics oxidized by ozone will be more polar than the original materials, by reason of the introduction of alcohol, aldehyde, and carboxylic acid groups. As a result, oxidized organics will be easier to flocculate with polyvalent cations or polyelectrolytes. For waters containing high levels of organics; therefore, ozonation during the earlier stages of treatment should be followed by addition of flocculating chemicals, then by coagulation, sedimentation, and/or filtration steps. To date, however, it appears that no experimental work has been done to confirm the above, and consequently, this is an area where future research should be directed.

For example, jar tests or small scale lab tests could be carried out to study the removal of specific organic by-products.

3.4 Solid-Phase Adsorption

Solid-phase adsorption, in the form of activated carbon for taste and odour control, has been in common use in water treatment for over 50 years. With the concern about trace organics in drinking water which has arisen in the past ten years, activated carbon is increasingly being used for removal of these substances.

The principle of the adsorption process is removal of an adsorbate from solution onto an adsorbent by means of physical and chemical attractive forces. In water treatment, the two main adsorbents used are granular activated carbon (GAC) and powdered activated carbon (PAC). More recently, ion exchange resins and polymeric adsorbents have drawn attention.

To date, little or no work has been done on removal of organic by-products resulting from ozonation by adsorption; however, based on research and application experiences over the past several decades, Weber (1983) concluded that activated carbon can function as an adsorbent for a substantial majority of potentially hazardous organic pollutants of current concern. It follows, therefore, that the adsorption process has a good potential for removing/reducing ozone by-products.

The significant properties of organic compounds which affect their uptake from aqueous solutions by activated carbon are reasonably known and quantifiable (see Weber, 1983, Chapter 7, page 5). Some general observed trends in carbon adsorption, reported by Benedek and Bancsi (1977), and Weber (1983) are:

- Compounds of low molecular weight and polar nature are not adsorbed well; conversely, higher molecular weight, less polar compounds, aromatic, and substitute aromatic species, pesticides, PCB's, and PAH's are strongly and extensively adsorbed, i.e. less soluble materials are more readily adsorbed.
- Increasing molecular weight favours adsorption until a limiting value is reached.
- A decrease in pH can, for some compounds, increase adsorption. This effect can be applied to removal of phenoxy acid herbicides.
- The oxygen content of the activated carbon can affect the ability to remove polar compounds such as p-nitrophenol.
- The number and size of the pores in activated carbon influence the ability of the carbon to remove specific compound types. For example, large molecules, such as lignins, require large pores for efficient adsorption.

While the above trends give a preliminary indication of how effective carbon adsorption may be, treatability studies specific to each particular water treatment situation will be required. These studies will determine the rates and capacities of adsorption. The studies should be carried out under different conditions in order to determine the effect of variables such as:

temperature
contact time
pH
staging effects
regeneration rates
pre-/post-treatment requirements

Further details of carbon adsorption studies have been provided by Weber (1983).

3.5 Biological Activity

One important benefit of ozonation is that it makes organic compounds more biodegradable (Bourbigot and Dore, 1982). It has been found that ozonation prior to slow sand or riverbank filtration and activated carbon columns can increase the elimination, by biological means, of some of the organic substances. For example, in Europe, it has been reported that some 65% to 75% of the organic material in the Rhine can be removed by biological degradation during river bank filtration. Biologically activated carbon columns, properly designed and operated, can greatly extend the period of carbon column performance. The above processes, extensively developed in Europe in the 1960's, are now in widespread use there.

3.6 Gas-Phase or Air Stripping

Air stripping is not a commonly used unit process in water treatment in Canada. The process consists of bringing water and air in contact with each other for the purpose of removing or transferring volatile substances from the water. Air stripping has been used to remove soluble gases such as hydrogen sulphide, methane, and carbon dioxide from groundwaters. It has also been used to reduce the concentration of taste and odour-producing compounds in water. More recently, air stripping has been used to reduce volatile organic compounds (VOC's) in water (McKinnon and Dyksen, 1984).

In 1980, McCarty reported that air stripping showed potential for removal of a large number of organic contaminants found in raw water. He stated that the potential of a compound for removal by air stripping could be predicted fairly accurately using Henry's Law constant (H atm m^3/mol).

Henry's constant is equal to:

$$H = \frac{P}{C}$$

where P = the vapour pressure of the compound (atm)
 C = the compound's solubility in water (moles/ m^3)

A high value of H indicates that a compound is susceptible to stripping. McCarty found that compounds with a value of H greater than about 0.001 atm m^3/mol were susceptible to air stripping.

Values of H for ozone by-products are not readily available, and calculation of H is beyond the scope of this report; however, since it is known that the by-products of ozonation would be highly oxygenated, this would tend to make them more soluble and result in low values of H . As a result, air stripping would not appear to have great potential for ozone by-product removal. Clearly, any future research should first focus on calculation of H for a number of ozone by-products to confirm the above hypothesis. In the unlikely event that air stripping is found to be a viable process, subsequent research should advance to other factors which affect air stripping, such as contact time, air to water ratio, and temperature.

3.7 Reverse Osmosis

The principle of reverse osmosis is the removal of molecules and ions from solution by means of filtration through a semi-permeable membrane. This is in contrast to rapid sand filtration and microfiltration, where only insoluble particles are removed.

Although the basic principle of reverse osmosis has been known for hundreds of years (Applegate, 1984), it was not until the 1960's, with the development of synthetic membranes, that this process became practical. At present, in water treatment, reverse osmosis is used for removal of inorganic substances from sea water and brackish water.

For organics removal, the effectiveness of reverse osmosis varies with the specific compound being removed. Nusbaum and Riedinger (1980) indicate that, in general, low molecular weight (below 200), non-polar, water soluble species tend to pass through current commercial membranes, and due to preferential passage, may even enrich the permeate. Examples are phenols, low and high molecular weight chlorinated hydrocarbons, and other halogenated species, pesticides, and low molecular weight alcohols; all compounds of particular concern in water treatment. In contrast, large complex organic substances, such as colour molecules, are almost completely removed.

Current membranes are capable of removing specific organic by-products. In the future, new membranes may be tailored to remove/eject other substances.

3.8 Summary of Findings

- (a) Little direct work has been done on the removal of ozonated organic by-products, but some indications of by-product removal may be obtained from work done on removal of chlorinated organic by-products.
- (b) Indications from the chemistry suggest that ozone reaction by-products should be more amenable to treatment by coagulation/flocculation and subsequent solids separation.
- (c) The reaction by-products should be more biodegradable, consequently GAC could become more effective due to rejuvenating active sites.
- (d) The reaction by-products will tend to have lower molecular weights and be more water soluble than the original organics; therefore, processes such as reverse osmosis will be less effective following ozonation.

CHAPTER 4

HEALTH SIGNIFICANCE OF BY-PRODUCTS

CHAPTER 4

HEALTH SIGNIFICANCE OF BY-PRODUCTS

4.1 Introduction

The objective of this chapter is to review what is known about the health effects of the by-products formed during ozonation of water.

As previously discussed, ozonation of water can result in the formation of a multitude of by-products; therefore, this chapter also discusses the application of screening tests.

4.2 Health Significance of Specific By-Products

Although the eventual outcome of the reaction with ozone should be the breakdown of the organic compounds to carbon dioxide, water, and inorganic anions (such as chloride ion), practical limitations in the amount of ozone applied and the reaction time available result in the formation of by-products. Due to varying factors - the complexity of ozone reactions (recall the various possibilities arising from direct or indirect reactions), the wide variety of organics which can be found in water, varying ozone dosages and reaction time, etc. - a complete catalogue of the by-products and their health effects will probably not be possible. Even so, a large number of compounds have been identified as resulting from ozonation of drinking water. Listings of these appear in reviews such as NRC (1980). A summary of the by-products and the results of health-effects testing are given in Appendix A (Table A.1).

From a health perspective, the most important process in water treatment is disinfection. In most areas, chlorine has been the disinfectant of choice, although ozone has been employed in a significant number of water treatment plants, especially in Europe. The appearance of an increasing number of studies describing the formation of chloro-organics during chlorine disinfection, and the possible adverse health effects which could occur as a result of their

ingestion, has led to an increased interest in alternate disinfectants, including ozone.

As a disinfectant, Carmicheal et al. (1982) report that ozone is probably superior to chlorine in terms of contact time and amount needed for the disinfection of all micro-organisms; however, it should be noted that ozone does not provide an effective residual disinfectant.

During the review of ozone reactions in water treatment, presented in Chapter 1, it became apparent that the reactions involved are varied and complex. This is similar to the case which presents itself in the use of chlorination for disinfection.

Cotruvo (1982) states that there is a great amount not known about the chlorinated or brominated by-products resulting from chlorination. Indeed, Cotruvo estimates that, on a mass balance balance, the organochlorine products produced account for only a few percent of the added chlorine and that there is a whole host of by-products for which little is known as to their identity or toxicology. When one considers that the chlorination of water has probably been more thoroughly studied than that of the ozonation of water, and that the analytical chemistry of chlorinated by-products is better developed than for ozonated by-products, it must be concluded that the situation as to the extent of our knowledge of the ozonated by-products is limited and will remain so for some time to come.

A method for avoiding the difficulties posed by the lack of knowledge on the identity and health effects of each and every by-product is to develop a method for testing the quality of the water produced by a process as a whole.

4.3 Mutagenicity and Carcinogenicity Testing of Water

As noted in the previous section, a method or combination of methods which could measure the health quality of water would be useful, especially as the knowledge of the by-products of ozonation is incomplete. The types of testing which could

be employed include acute toxicity tests (e.g. LD50's), carcinogenicity screening tests (e.g. Ames tests), and long-term animal testing.

The acute toxicity testing would usually not be needed as it is not expected that ozonation would produce an acutely toxic (i.e. toxic in the "short term") water. The third type of test, long-term animal studies, is quite cumbersome and costly in terms of manpower and resources.

Mutagenic tests, or other types of screening tests, are probably most applicable to a water treatment situation. Even these may have some drawbacks. Although Ahmed and Dominiquez (1982) report that they are relatively economical in terms of time (two weeks to months) and cost (\$350 to \$5,000), this is still of a longer time frame than that of a water treatment process (typically accomplished in hours). This means that a screening type test (or a long-term test) will only provide an assessment of the long-term water quality. Still, if the raw water quality and the treatment scheme do not vary appreciably, screening tests have potential.

4.4 Results of Mutagenic Screening Tests

Spanggord and McClurg (1978), and Simmon et al. (1978) have attempted to evaluate the potential biological hazard resulting from ozonation of aqueous solutions of some selected organics through the use of rapid microbiological assays (see Table A.1) before and after ozonation. These authors also attempted to identify the by-product responsible for the biological activity, where possible. It should be noted that the concentrations of substrates used were not chosen to mimic water treatment conditions but to provide sufficient amounts of material for the Ames test for mutagenicity. Of the compounds tested, ethanol, 1,1-diphenylhydrazine, nitrilotriacetic acid, phenol, and benzidine showed some mutagenic activity after ozonation but not before ozonation. Of the other compounds tested, Simmon et al. (1978) noted that some are known mutagens, e.g. benzo(a)pyrene, but not at the concentrations used. This work by Spanggord and McClurg, and by Simmon et al. illustrated three points:

- (a) Mutagenic activity is a function of concentration.

- (b) Mutagenic activity was related to the extent of ozonation. One compound, 1,1-diphenylhydrazine, was not mutagenic after exhaustive ozonation but was mutagenic after 60 minutes of ozonation.
- (c) Mutagenic activity, and thus, the level of carcinogenicity as indicated by the 85% to 96% correlation of mutagenicity to carcinogenicity for individual compounds (Ahmed and Dominquez, 1982), can increase as a result of ozonation.

Two papers published by a group of investigators at the National Institute for Water Supply of the Netherlands (Zoeteman et al., 1982; Kool et al., 1982) discuss the mutagenic activity associated with disinfection (by chlorine, chlorine dioxide, ozone, and UV-irradiation) and the presence, introduction, and removal of mutagenic activity from drinking water in the Netherlands. Zoeteman found that both chlorine and chlorine dioxide disinfection caused an increase in levels of direct acting mutagens in Rhine River water, as measured using *Salmonella Typhimurium* TA98. Ozonation caused a decrease in mutagenicity. UV irradiation did not cause a change in activity. During the investigation, it was observed that coagulation/filtration with FeCl_3 and carbon filtration each caused a reduction in mutagenicity in water which had been treated with chlorine dioxide. Although Zoeteman's results indicate that ozone causes a decrease in the mutagenic activity of the Rhine River water, he does point out that the identity of the mutagens was not known, that the change in mutagenic activity may be affected by the use of XAD resin (since the adsorption behaviour of the mutagens is not known, it is possible that ozonation, or any chemical process, can produce mutagens which do not extract with XAD resin). The raw water itself, however, possessed considerable activity, and in many cases, the level resulting from disinfection was less than the level present in the raw water.

Kool et al. (1982) report the results of an 18-city survey where water is drawn from the Meuse and Rhine Rivers. These cities prepare their drinking water from ground, river, or a combination of ground and river waters. The water is drawn from the sources by a variety of methods:

- as surface water
- from ground water
- by dune infiltration
- by bank infiltration

It was found that only two out of five cities using ground water showed marginal mutagenic activity in their water. Of the 15 cities that drew their water from surface sources directly or by infiltration, 12 showed activity. The occurrence of activity seemed to be dependent on the type of treatment rather than source. It was found that:

- (a) Breakpoint chlorination increased the direct acting mutagenic activity.
- (b) Activated powdered carbon reduces activity somewhat.
- (c) Ozonation had a marginal effect on activity.
- (d) Activated carbon filters are effective in reducing activity.
- (e) The sequence of dune infiltration in combination with powdered activated carbon and slow sand filtration was very effective in reducing activity.

Kool et al. (1982) also briefly discuss the significance of mutagenicity of water to health. They point out that more research is needed and that long-term animal studies with drinking water concentrates, as well as additional in vitro assays and chemical analyses, are being performed on the mutagenic fractions extracted from water to obtain a better understanding of their health significance.

Bull et al. (1982) have discussed the use of biological assay systems to assess the relative carcinogenic hazards of disinfection by-products. Bull et al. (1982) used mouse skin initiation/promotion studies. In the testing, the mice were injected with a tumour initiation dose of 150 mg/kg of a water extract. The water extract was prepared by a reverse osmosis concentration of drinking

water, resulting in a several hundred-fold concentration from the original volume (usually 400-fold). After the injection period, a promoter was applied to the skin of each mouse for a period of 20 weeks. During the testing period, the mice were examined for papillomas. Papillomas are non-malignant tumours and not life threatening in themselves, although Bull et al. (1982) cite Burns and Albert (1982), who report that, while carcinomas can arise from or be independent of papillomas, the number of papillomas which arise are predictive of later carcinoma development. This was also observed by Bull et al. (1982), who found a general increase in carcinomas in groups of mice having more papillomas.

Bull et al. (1982) tested the tap water from five U.S. cities with a variety of raw water sources. The cities were Ottumwa (surface water with agricultural runoff), Miami (ground water), Philadelphia (surface water with municipal waste), New Orleans (surface water with industrial waste), and Seattle (pristine water from a protected watershed). In the mouse skin initiation/promotion tests of the extracts from the above tap waters, the tumour response was higher than that found for two control samples, although only the Ottawa tap water was statistically significantly different from the control. The results obtained were taken (Bull et al., 1982) to show that compounds with carcinogenic activity were present in the water. Details of the water treatment schemes used in these five cities were not reported.

In the same study, waters which had been treated with four different disinfectants, specifically chlorine, chlorine dioxide, chloramine, and ozone, were concentrated and subjected to the same mouse skin initiator/promoter test. Extracts from chlorine, chloramine, and ozone disinfected waters each caused an increase in tumour incidence in the test animals; however, upon two further repetitions of the same test (to assess the reproducibility of the results), the extracts from the non-disinfected water were found to induce tumours in the mice at approximately the same level as the disinfected waters. This variability in the results obtained by Bull et al. (1982) is noteworthy.

Despite the variability of the results found by Bull et al. (1982), the results are significant since they show that tumour induction can occur in an intact animal model.

4.5 Summary of Findings

- (a) Further development of a procedure or a combination of procedures to assess the overall health quality of water which has been ozonated is necessary. Overall (or screening) tests are needed since all by-products produced by ozonation of raw water have not been identified and evaluated for their impact on health.
- (b) In the application of a screening test, it is necessary to compare the quality of the raw water to the finished water.
- (c) The screening test procedures, which have been reported in the literature, usually involve examining the quality of water obtained by ozonating a much higher concentration of a compound than normally found in raw waters or examining a concentrated extract. Since this can affect the results obtained, further work should be undertaken to define the effect of this on the results.
- (d) As measured by the use of mutagenicity testing of water, various workers have observed that mutagenicity can increase, decrease, or remain relatively unchanged as a result of ozonation.
- (e) It has been reported that the level of mutagenic activity of water is a function of the extent of ozonation, i.e. ozonation results in an increase in mutagenicity to a peak value followed by a decrease as the ozonation continues.

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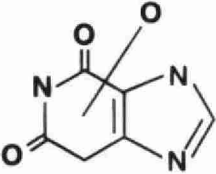
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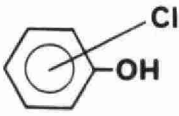
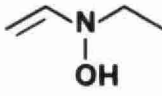
APPENDIX A

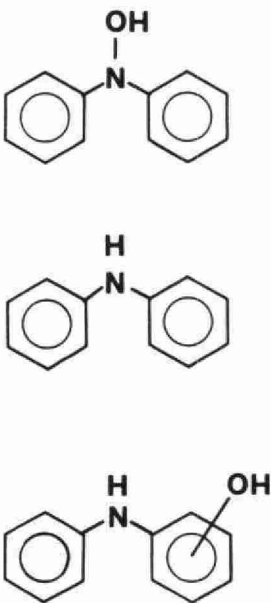
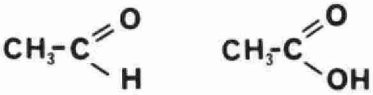
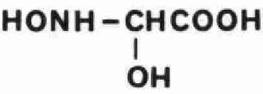
OZONATION PRODUCTS FOR SELECTED ORGANICS

TABLE A.1

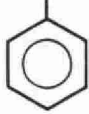

Ozonation Products for Selected Organics


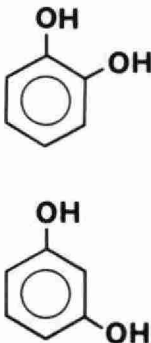
COMPOUND ^{a,b}	PRODUCTS	BIOASSAY	COMMENTS
Aldrin		NMO ^c	low pH
Benzene	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HC} - \text{CH} \end{array}$ $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HOC} - \text{CH} \end{array}$ $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO-C} - \text{C-OH} \end{array}$		
Benzidine, hydrochloride salt		mutagenicity increased	
Benzoic acid		NMO	pH < 4.5
Caffeine		NMO	low pH

COMPOUND ^{a,b}	PRODUCTS	BIOASSAY	COMMENTS
Chlorobenzene	 $\text{HOOC}\underset{\text{OH}}{\text{CH}}\text{CH}(\text{Cl})\text{COOH}$ plus ring opened products as for chlorophenols		
DDT		NMO	low pH
2,4-dichlorophenol	$\text{HCOOH} \quad \text{HOOC}-\text{COOH} \quad \text{Cl}^-$		
2,4-dichlorophenol	$\text{CH}_3\text{-COOH} \quad \text{HCOOH}$ $\text{OHC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$		
Diethylamine	$\text{CH}_3\text{CH}=\text{NOH}$ 	NMO	pH 11.1

COMPOUND ^{a,b}	PRODUCTS	BIOASSAY	COMMENTS
Diphenylhydrazine		weakly mutagenic after exhaustive ozonation	pH 7
2,4-dinitrotoluene		NMO	low pH
Ethanol	 <p>and other unidentified products</p>	mutagenic after ozonation	pH < 5
Glycine		NMO	low pH

COMPOUND ^{a,b}	PRODUCTS	BIOASSAY	COMMENTS
Humic acids	$\text{HOOC-CH}_2\text{-COOH}$ $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ $\text{HOOC-(CH}_2)_2\text{COOH}$ $\text{CH}_3(\text{CH}_2)_5\text{COOH}$ $\text{C}_6\text{H}_5\text{-COOH}$ $\text{CH}_3\text{-(CH}_2)_6\text{-COOH}$ $\text{HOOC-(CH}_2)_3\text{-COOH}$ $\text{HOOC-(CH}_2)_4\text{-COOH}$ $\text{HOOC-(CH}_2)_5\text{-COOH}$ $\text{HOOC-(CH}_2)_6\text{-COOH}$ $\text{HOOC-(CH}_2)_7\text{-COOH}$ $\text{HOOC-(CH}_2)_8\text{COOH}$ $\text{HOOC-}\underset{\text{H}}{\text{C}}\text{(CH}_2\text{COOH)}_2$	NMO	low pH

COMPOUND ^{a,b}	PRODUCTS	BIOASSAY	COMMENTS
Nitrilotriacetic acid; sodium salt		slight increase	pH 10 (approx.)
Oleic acid	$\text{C}_8\text{H}_{17}\text{C} \begin{array}{l} \text{=O} \\ \text{-OH} \end{array}$ $\begin{array}{c} \text{O} \\ \text{=C} \end{array} (\text{CH}_2)_7 \begin{array}{c} \text{O} \\ \text{=C} \end{array} \text{OH}$ $\begin{array}{c} \text{O} \\ \text{=C} \end{array} (\text{CH}_2)_7 \begin{array}{c} \text{O} \\ \text{=C} \end{array} \text{OH}$	NMO	pH < 6
PCB mixture	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> COOH  Cl^- </div> <div style="text-align: center;"> COOH  H_2O_2 </div> </div>		

COMPOUND(a) (b)	PRODUCTS	BIOASSAY	COMMENTS
Phenanthrene			
Phenol		toxic products present; weakly mutagenic	pH < 7
Pyrene	CH_3COOH CO_2 $\text{HOOC} - \text{COOH}$		

COMPOUND ^{a,b}	PRODUCTS	BIOASSAY	COMMENTS
1,3,5-trimethylbenzene	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CH}_3-\text{C}-\text{CH} \quad \text{HCOOH} \end{array}$ CH_3-COOH		

- a. Some compounds have multiple entries due to different results sustained by various workers under different conditions.
- b. Duplicate entries may arise since different workers may obtain different results.
- c. No mutagenicity observed.

APPENDIX B
WORK PROGRAM

APPENDIX B

WORK PROGRAM

To provide a detailed technical report to the Environmental Technology Section, Laboratory Services & Applied Research Branch, Ontario Ministry of the Environment, in the use of ozone in drinking water treatment. Detailed work plan below:

Detailed Work Plan

1. Provide an in-depth literature review of state-of-the-art use of ozone in drinking water treatment.
2. Examine and report on expected reactions/by-products with typical components at ambient levels ($\mu\text{g/L}$) from the following classes:
 - halogenated aliphatics
 - chlorinated benzene and toluene derivatives
 - aromatic solvents
 - chlorinated pesticides
 - PCB's
 - chlorinated phenols
 - PAH's plus methyl and chloro derivatives
 - phthalate esters
3. Assess the theoretical feasibility of removal or reduction methodologies of reaction by-products, etc.
4. Preliminary assessment of any health significance of these by-products at their expected ambient level (mg/L).
5. Address, in detail, gaps in ozone technology use in drinking water to enable an effective assessment of future research directions.

6. Prepare a written report (ten copies), acceptable to the Ontario Ministry of the Environment, detailing the above aspects by 31 March 1984. (Extended to 31 December 1984.)



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